SCIENCE FOR GLASS PRODUCTION

UDC 666.112.2:666.113.33'22'21'.001.6

SPECIFICS OF SYNTHESIS OF SOLUBLE GLASS USING SODIUM SULFATE

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Translated from Steklo i Keramika, No. 9, pp. 10 – 13, September, 1999.

Soluble glass is synthesized using sodium sulfate. Decorative glass ceramic materials are made on its basis. This paper considers the results of x-ray phase analysis and thermodynamic calculations of the redox reactions of sodium sulfite formation, as well as data on physicomechanical and color testing of the produced composite materials.

The current situation calls for the development of resource-saving technologies for producing various silicate materials. Of special interest is the method for producing soluble glass using the sulfate technology. At present, this product is manufactured according to the traditional sodium bicarbonate technology. However, Na_2CO_3 is an expensive material. Therefore, it is expedient to replace calcined soda with a less expensive component, i.e., sodium sulfate Na_2SO_4 (a chemical industry waste), which would ensure the required quality and properties in soluble and liquid glass. Sulfate wastes are accumulated in considerable quantities, which deteriorates the ambient environment. The authors investigated the possibility of using sodium sulfate in soluble glass production.

Liquid glass is widely used in many sectors of economics (construction, machine building, metallurgy, paper-and-pulp industry, etc.)

Sodium sulfate wastes from the Volgodonsk Chemical Works and the Novocherkassk Synthetic Product Works, as well as sand from the local quarry, were used for the purpose of obtaining alkaline silicates in the $Na_2SO_4 – SiO_2$ system. The chemical compositions of the materials are listed in Table 1.

The redox processes in the formation of a silicate block are of special interest for the development of sulfate technologies. The reaction of sodium sulfate with silica, which produces $Na_2O \cdot nSiO_2$ in glass melting in oxidizing conditions, occurs only in the region of high temperatures (about 1450°C), which is supported by the thermodynamic calculations of Gibbs free energy and the equilibrium constant of the reaction:

$$Na_2SO_4 \rightarrow Na_2SO_3 + 1/2O_2. \quad (1)$$

Sintering of a mixture in an oxidizing gas medium with the excess-air coefficient equal to 1.1 – 1.3 results in the emission of 2 – 4% oxygen in waste gases.

In order to transform sodium sulfate Na_2SO_4 into sulfite Na_2SO_3, reducing conditions should be provided in the zone of the mixture sintering. These conditions can be achieved by introducing carbon-containing additives into the mixture (carbon, hydrocarbon compounds, sawdust). As the mixture containing these additives is heated, the reducing reactants CO and H_2 are formed, which ensures the following reactions:

$$Na_2SO_4 + CO \rightarrow Na_2SO_3 + CO_2; \quad (2)$$

$$Na_2SO_4 + H_2 \rightarrow Na_2SO_3 + H_2O. \quad (3)$$

In order to substantiate the probability of reactions (1) – (3), thermodynamic calculations of the enthalpy ΔH^0, entropy ΔS^0, free energy ΔG^0, and the equilibrium constant

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TABLE 1

Material	Mass content, %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	organic impurities	calcination loss
Sodium sulfate (waste)	2.30	0.30	0.12	1.20	43.08	16.00	37.00
Sand	98.55	1.20	0.25	–	–	–	–

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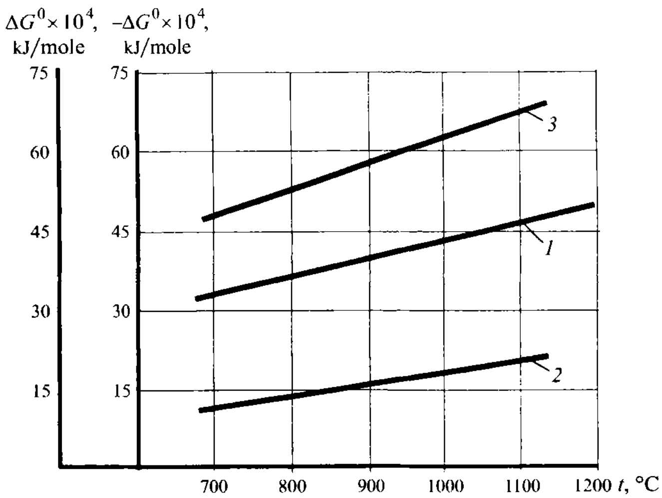

Fig. 1. Free energy ΔG^0 as a function of soluble glass melting temperature t: *1*) oxidizing conditions of synthesis; *2, 3*) reducing conditions of synthesis.

K were carried out for the temperature interval of 700 – 1200°C.

$$\Delta H^0 = \Delta H + \int_{T_1}^{T_2} \Delta C_p \, dT;$$

$$\Delta S^0 = \Delta S + \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT;$$

$$\Delta G = \Delta H^0 - T\Delta S^0;$$

$$\lg K = -\frac{G^0}{23RT}.$$

The reaction of Na_2SO_4 with oxygen in sintering proceeds in the solid phase. The calculation of the thermodynamic parameters as a function of heat capacity $C_p = f(T)$ is based on numerical values of activities [1, 2]:

$$C_p = a + bT,$$

where a and b are the activities of Na_2SO_4 and Na_2SO_3.

The difference in activities $\Delta\ a$ and $\Delta\ b$ for reactions (1) – (3) can be determined from the equations:

$$\Delta a = a_{Na_2SO_3} + \frac{1}{2} a_{O_2} - a_{Na_2SO_4} = -0.22;$$

$$\Delta b = b_{Na_2SO_3} + \frac{1}{2} b_{O_2} - b_{Na_2SO_4} = 0.$$

Whence it follows that

$$\Delta C_p = -0.22;$$

$$\Delta a = a_{Na_2SO_3} + a_{CO_2} - a_{Na_2SO_4} - a_{CO} = -0.02;$$

$$\Delta b = b_{Na_2SO_3} + b_{CO_2} - b_{Na_2SO_4} - b_{CO} = 0.62 \times 10^{-3}.$$

Therefore,

$$\Delta C_p = -0.02 + 0.62 \times 10^{-3} T;$$

$$\Delta a = a_{Na_2SO_3} + a_{H_2O} - a_{Na_2SO_4} - a_{H_2} = -3.02;$$

$$\Delta b = b_{Na_2SO_3} + b_{H_2O} - b_{Na_2SO_4} - b_{H_2} = 1.18 \times 10^{-3}.$$

Whence it follows that

$$\Delta C_p = -3.02 + 1.18 \times 10^{-3} T.$$

The thermodynamic calculations of numerical values ΔH^0, ΔS^0, ΔG^0, and K are presented in Table 2.

As is seen in Table 2 and Fig. 1, the free energy ΔG^0 in reaction (1) in sintering under oxidizing conditions has positive numerical values, which indicates that the reduction of sodium sulfate to sulfite is impossible. In contrast to this, in a reducing gas medium, the energies ΔG^0 in reactions (2) and (3) have increased negative values, which is indicative of intense reduction of sodium sulfate to sulfite.

The change in the phase composition and the structural specifics of the soluble glass mixture minerals were studied by x-ray phase analysis (Fig. 2). The samples were cakes sintered at a relatively low temperature (1000°C), as well as soluble glass samples melted at the temperature of 1350°C. The x-ray patterns of the samples obtained in the reducing medium (Fig. 2*a* and *b*) exhibit the diffraction maxima corresponding to the following oxides and compounds: Na_2O, SiO_2, $Na_2O \cdot SiO_2$, and $Na_2O \cdot 2SiO_2$ (d = 1.747, 1.786, 3.807, and 4.270 Å).

TABLE 2

Reaction	Temperature, °C	ΔH^0, kJ/mole	ΔS^0, kJ/K	ΔG^0, kJ/mole	K
		Oxidizing gas medium			
1	900	2430.437	– 340.806	402195.3	– 7.8 × 10^{17}
	1200	2454.109	– 341.224	504777.4	– 7.6 × 10^{17}
		Reducing gas medium			
2	700	2182.160	30.98232	– 27963.6	31.6
	800	2704.673	16.32852	– 14815.8	5.6
	900	3279.520	16.74720	– 16364.9	5.4
	1000	3905.866	17.16588	– 17946.3	5.5
	1100	3251.050	18.00324	– 21467.4	6.5
3	700	– 4243.320	45.63612	– 48647.3	398.1
	800	– 4497.040	45.21744	– 53015.4	389.1
	900	– 4651.950	45.21744	– 57692.0	380.2
	1000	– 4708.060	45.63612	– 62802.8	371.5
	1100	– 4664.930	45.63612	– 67323.3	371.5

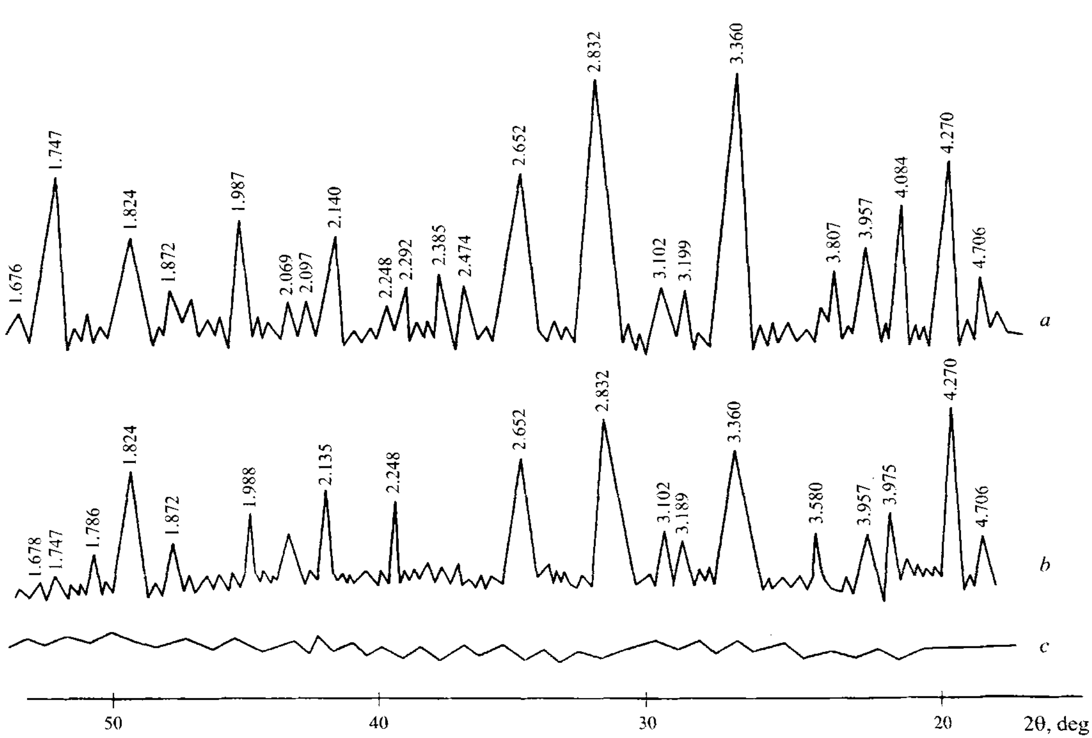

Fig. 2. X-ray patterns of samples: *a* and *b*) the sinters of $SiO_2 - Na_2SO_4$ mixtures with and without hydrocarbon additives, respectively; *c*) synthesized soluble glass.

The glass melted in an oxidizing medium up to temperature 1200°C does not exhibit interplanar bands typical of alkaline silicates. This is an indication of the fact that sulfite Na_2SO_3 is not formed in the absence of reducing additives.

No crystal phases were identified in the x-ray pattern of the finished glass (Fig. 2*c*). This points to the amorphous structure of the material and the completion of the melting process. The results of the analysis confirm that the soluble glass produced using the proposed technology does not differ in its properties from glass produced using the traditional technology based on soda.

The silicate block was used to produce liquid glass that was employed in production of glass ceramic decorative non-fired composite materials. The materials were synthesized from red brick waste, refractories, glass, and limestone-carbonate waste from a thermal power plant, which were milled to a specific surface area of 4500 cm^2/g. The chemical composition of these wastes allows for the formation of calcium-aluminosilicate minerals in the $CaO - Al_2O_3 - SiO_2$ system. Ferrous oxide pigments (aluminum production waste, red iron ore, and redoxide) were used to obtain decorative glass ceramics.

TABLE 3

Mixture	Milled materials	Composite material composition, %	Pigment		Color parameters			Reflection coefficient, %	Compressive strength, MPa
			type	quantity, %	λ, nm	*p*, %	ρ, %		
1	Red brick	60	–	–	483	30	56	67	25
	Clear glass	25							
	Liquid glass	5							
	Limestone-carbonate waste	10							
2	Aluminosilicate waste	75	Red iron ore	10	595	43	61	54	18
	Liquid glass	5							
	Limestone-carbonate waste	10							
3	Aluminosilicate waste	78	Chromium oxide	2	487	38	59	56	20
	Liquid glass	5							
	Limestone-carbonate waste	15							
4	Aluminosilicate waste	80	–	–	610	91	82	82	23
	Liquid glass	5							
	Limestone-carbonate waste	15							

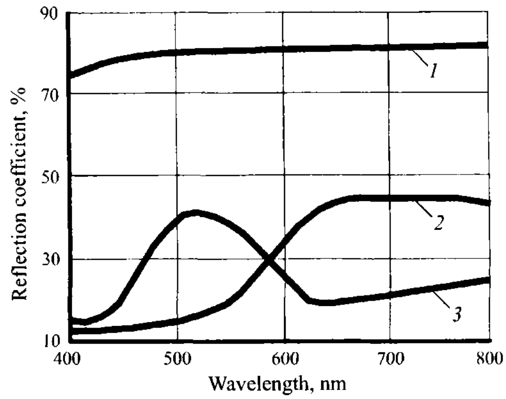

Fig. 3. Spectral reflection curves of composite materials: *1*) white (Table 3, mixture 4); *2* and *3*) reddish-brown and green, respectively.

The physicochemical and the color tests of glass ceramic materials are presented in Table 3 and Fig. 3.

The testing of the color parameters of the composite materials revealed that the decorative materials based on milled red brick have a light pink shade, and the articles containing oxidized iron ore or redoxide (up to 0.5%) acquire reddish-brown shades over a wide color spectrum.

An intense green color in the composites was attained by adding technical grade chromium oxide (Cr_2O_3).

The use of aluminosilicate waste with an increased reflection coefficient makes it possible to obtain composites of special whiteness, which allows for expressive architectural effects.

The resulting products have satisfactory strength parameters (18 – 25 MPa), which satisfies civil engineering requirements.

Liquid glass based on the synthesized silicate block was used to produce nonfired decorative glass ceramic composites which are architecturally expressive and durable.

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